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## AN ATOMISTIC MODEL OF SOLUTE TRAPPING

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### ABSTRACT

An atomistic model for nonequilibrium solute segregation during rapid solidification is presented in terms of a single unknown parameter, the interfacial diffusivity  $D_i$ . The results for stepwise growth and for continuous growth at the same interface velocity differ quantitatively but exhibit the same qualitative features. A transition from equilibrium segregation to complete solute trapping occurs over approximately an order of magnitude in growth velocity, as the interface speed surpasses the maximum speed with which solute atoms can diffuse across the interface to remain ahead of the growing crystal. This diffusive speed is given by  $D_i/\lambda$ , where  $\lambda$  is the interatomic spacing, and is typically of the order 10 meters per second. A solute drag term and an intrinsic interfacial mobility term are included in an equation which predicts the growth velocity of a planar interface. Steady-state solutions are presented for the Ag-Cu system.

### INTRODUCTION

Experiments have shown [1,2] that the chemical potential of the minor component of a binary alloy often increases during rapid solidification. This result rules out concepts of local equilibrium and independence of atomic species. In this paper, a simple model is described which predicts suppressed segregation as the solidification velocity becomes faster than the diffusive speed of solute across the interface.

Conventional modelling of interface kinetics uses the same atomic motions to describe crystallization as those to describe interdiffusion. In such a case, the growth speed  $u$  can never exceed the maximum diffusive speed  $D_i/\lambda$ , where  $D_i$  is the diffusion coefficient at the interface and  $\lambda$  is the interatomic distance. However, the collision-limited growth model developed by Turnbull and coworkers [3-10], which has recently been confirmed by Broughton et. al. [11] indicates that for metallic systems such a scaling is invalid and that  $u_c$ , the speed of sound, should be the only limit to the crystal growth rate. Consequently the growth speed can easily exceed the diffusive speed by a large factor, and when it does so in alloys we expect suppressed solute segregation and a diffusionless transformation.

The reason that crystal growth in metals should not scale with diffusion is illustrated in Fig. 1. A crystallization event consists of an atom shifting its position a small distance to move from a potential well in the liquid structure to a well on the crystal lattice. Since no bonds must be broken, the activation barrier for this reaction ought to be quite small; in the Turnbull collision-limited growth model this barrier is zero. A diffusive jump, on the other hand, is a different atomic process in this system. Position shifts of a fraction of an interatomic distance do not accomplish the solute-solvent redistribution which is necessary to avoid solute incorporation into the crystal. A solute atom must accomplish three things to avoid crystallization: It must escape from its potential well, as shown by the dashed arrow in Fig. 1, as the energy of the well increases and the well moves to the lattice site. It must push solvent atoms out of the way. And it must be replaced by a solvent atom on the lattice site, or else it will be pushed right back to where it came from.

Atoms in the interface region tend to interdiffuse in order to establish equilibrium compositions on either side of the interface. As the interface passes, solute-solvent redistribution only occurs during a limited time. Before the interface arrives, the driving force for redistribution is zero; afterwards, atomic mobilities are too low to permit significant interdiffusion. When  $u \ll D_i/\lambda$ , there is plenty of time for the atoms at the

interface to equilibrate. As the growth velocity becomes greater, solute and solvent atoms have less time while they are in the interface region to interdiffuse and maintain local equilibrium. When  $u \gg D_i/\lambda$ , the atoms have no time to interdiffuse; the interface passes and locks the liquid composition into the bulk of the solid before the atoms have a chance to react.

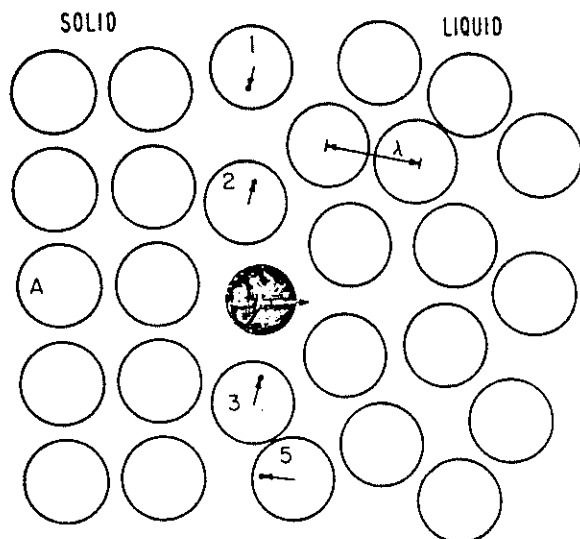


Fig. 1 Choreography of Solute Trapping. In order to avoid incorporation into the crystal (solid arrow), the "B" atom must:  
1) ESCAPE from its potential well (dashed arrow) as the well gains energy and moves to the lattice site (solid arrow),  
2) PUSH "A" atoms out of the way,  
3) BE REPLACED with an "A" atom on the lattice site.

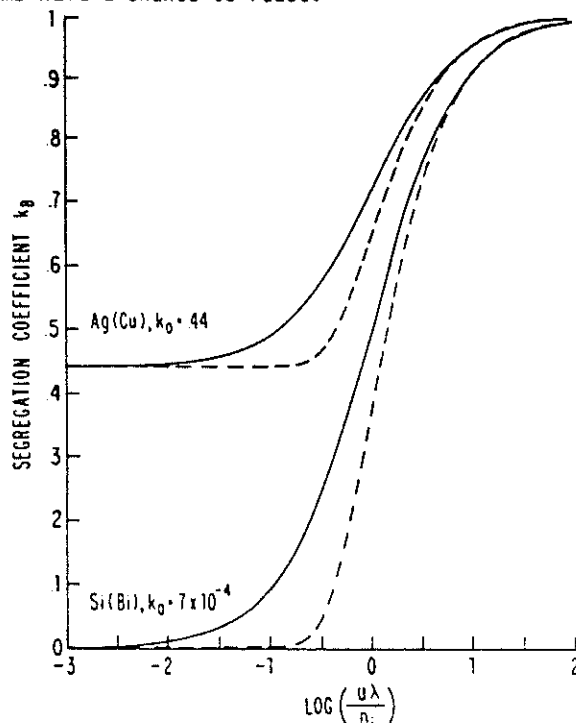


Fig. 2 Variation of segregation coefficient with dimensionless velocity, dilute solution limit. Dashed lines: stepwise growth model (equation 1). Solid lines: continuous growth model (equation 2).  $k_0$  is  $k_e$  for a dilute solution; i.e.  $k_e$  at the melting point of pure solvent.

#### SOLUTE TRAPPING MODEL

The mathematical derivation and extensive discussion of the solute trapping model are published elsewhere [12]. A summary is given here of the assumptions that go into the modelling.

**Stepwise Growth Model.** If growth occurs by the rapid lateral passage of steps of height  $\lambda$ , then the average time between the passage of steps is  $\tau = \lambda/u$ , where  $u$  is the growth velocity. The time it takes solvent atoms to shift to their lattice positions is negligible when compared to  $\tau$ , and the shifts can be treated as virtually instantaneous. The interface is thus assumed to be planar and executing instantaneous jumps of length  $\lambda$  separated by a time interval  $\tau = \lambda/u$ . The jump of the interface is assumed to incorporate one liquid monolayer, including all solute atoms, into the crystal lattice. Solute diffuses back into the liquid during the interval  $\tau$ ; diffusive-style rate equations give the composition in the solid monolayer at the interface as a function of time. (The composition of the liquid at the interface is assumed to be constant and given by the solution to the diffusion equation in the bulk of the liquid.) Solute remaining in the solid monolayer at  $t = \tau$  is permanently buried into the bulk of the solid, where diffusion is negligible, by the advance of the interface across the next monolayer. The result for a dilute solution of B in A is

$$k_B(u, T) = k_e(T) + [1 - k_e(T)] \exp(-D_i/u\lambda), \quad (1)$$

where  $T$  is the interface temperature, the equilibrium segregation coefficient  $k_e(T)$  is the ratio of the solidus composition to the liquidus composition at the undercooled temperature  $T$ , and the interface diffusivity  $D_i$  is the only fitting parameter in the model. The result for the stepwise-growth model is plotted in Fig. 2, note that  $k_B \rightarrow k_e$  when  $u \ll D_i/\lambda$  and  $k_B \rightarrow 1$  when  $u \gg D_i/\lambda$ .

Continuous Growth Model. If continuous solidification occurs, the impurity atom is being dragged toward its lattice site during a time period of order  $\tau$ . The details are complex and unknown, but in the limit of strict steady-state fluxes on a microscopic scale, the problem simplifies. The fluxes and concentrations become time-independent and the same diffusive-style rate equations as before yield, for a dilute solution of B in A,

$$k_B(u, T) = [(u\lambda/D_i) + k_e(T)] / [(u\lambda/D_i) + 1] \quad (2)$$

This function is also plotted in Fig. 2.

## GROWTH VELOCITY

Equations (1) and (2) for solute trapping require information, either theoretical or experimental, for the velocity-undercooling function. In many cases the assumption of no interfacial undercooling is a useful one, but the assumption becomes unrealistic at high velocities and solute concentrations. A dissipation-theory treatment of the interfacial undercooling problem for alloys is used below.

For pure systems, the process is easily understood. In equilibrium, the crystallization reaction and the backward (melting) reaction are equal in magnitude. When there is a finite driving force for crystallization, the former exceeds the latter by a Boltzmann factor  $\exp(\Delta u/RT)$ ; the growth velocity is given by their difference. The kinetics are lumped into an intrinsic growth-velocity-limit,  $u_0(T)$ , which is the speed with which the interface would propagate at infinite driving force (i.e. when the back reaction disappears). The growth velocity is then written:  $u = u_0(T)[1 - \exp(-\Delta u/RT)]$ . This becomes the familiar  $u = M \Delta G$  at small driving forces. Inverting the above expression, we have  $\Delta u = RT \ln(1 - u/u_0)$ . The left-hand side is the driving free energy; the right-hand side can be thought of as the free energy dissipated by the irreversible crystallization reaction at the interface. Thus the velocity-driving force relation can be written  $\Delta G_{DF} = \Delta G_F$ , where  $\Delta G_{DF}$  is the driving energy, expressed as free energy per mole, and  $\Delta G_F$ , the "interface friction energy" due to a finite interfacial mobility, is the free energy dissipated per mole of material solidified. We say that the available driving force is dissipated by the irreversible processes at the interface.

For alloys, we can write

$$\Delta G_{DF} = \Sigma \Delta G_{DISS}, \quad (3)$$

where the  $\Delta G_{DISS}$  are the losses due to all of the dissipative processes going on simultaneously. In the steady state, this must hold: the driving free energy does no work on the surroundings and so it must be entirely dissipated by irreversible processes during the transformation. If we can calculate the dissipation and the driving force as functions of velocity, we have an equation which predicts the growth velocity. Ignoring heat conduction, the two dissipative processes at the interface are the aforementioned crystallization and redistribution reactions. The dissipative terms associated with them are, respectively, the "interface friction energy"  $\Delta G_F$  and the "solute drag"  $\Delta G_D$  [13,14]. By assuming interface friction to be the same for alloys as for pure systems, we can calculate these terms [15]. The results are  $\Delta G_F = RT \ln(1 - u/u_0)$  and, for the dilute solution continuous growth model (eq'n 2),  $\Delta G_D = X_s RT [(1 - k_B)/k_B] \ln[k_B/k_A(T)]$ . The driving force is given by [14]  $\Delta G_{DF} = X_s \Delta u_B + (1 - X_s) \Delta u_A$ ; the growth velocity equation becomes

$$\Delta G_{DF}(u) = \Delta G_F(u) + \Delta G_D(u) \quad (4)$$

It turns out that one of the dissipative terms is usually negligible compared to the other; the transition occurs over a very small velocity range. Consequently the equation can be simplified away from the transition. For e-beam melting experiments on Ag(Cu), with interface velocities in the centimeter-per-second to meter-per-second range,  $\Delta G_D$  dominates most of the time; for laser annealing of doped Si with meter-per-second velocities,  $\Delta G_F$  almost always dominates. During a diffusionless transformation in any system,  $\Delta G_D$  vanishes.

The dilute solution approximation is invalid when the mole fraction of solute is no longer negligible or when activity coefficients are no longer constants. When the appropriate corrections to the fluxes and driving forces in the continuous growth model are made [15], the results are

$$k_B = [(u\lambda/D_i) + X_o] / [(u\lambda/D_i) + 1 - (1 - X_o)X_{2i}], \quad (5)$$

$$\Delta G_D = X_s [(1 - k_B)/k_B] RT \ln[k_B/k_A X_o], \quad (6)$$

where  $X_o(X_s, X_{2i}, T) = \exp[-(\Delta(u_B^* - u_A^*)/RT)]$ ,  $u'(X, T) = u(X, T) - RT \ln X = u^0(T) + RT \ln \gamma(X, T)$ ,  $X_{2i}$  is the mole fraction in the liquid at the interface,  $k_A = X_A^A/X_{2i}^A$ , A = solute, B = solvent, and  $\Delta =$  "solid minus liquid". The implicit assumption has been made that at the interface the transition state behaves in an ideal manner. In practice, temperature and composition dependence may show up in  $D_i$ .

## RESULTS

Equations 4, 5, and 6 were solved numerically; some of the results follow. For the Ag-Cu system, the thermodynamic model of J. Murray [16] was used to obtain the chemical potential of Ag and of Cu across the phase diagram. The following parameters were used:  $\lambda = 2\text{\AA}$ ,  $u_0 = 340000\text{ cm/s}$ ,  $D_i = .00122 \exp[-(10\text{ kcal/mole})/RT]\text{ cm}^2/\text{s}$ . The results are plotted as interface temperature and compositions on the phase diagram in Fig. 3; we see that for a given composition  $X_{li}$  in the liquid at the interface, the solid composition increases and the interface temperature drops as the velocity is increased. In a steady-state e-beam melting experiment [17], the solid composition is constrained to be equal to the bulk liquid composition. The velocity is independently controlled; the dependent variables are  $X_{li}$  and  $T$ . The way they behave is shown in Fig. 4. As the velocity is increased, the liquid composition at the interface decreases due to solute trapping, and the interface temperature actually rises, trying to follow the liquidus. When the  $T_0$  line is reached, a diffusionless transformation becomes thermodynamically possible. However, diffusionless solidification does not commence until some distance beyond the  $T_0$  line, when the velocity is great enough to suppress the redistribution reaction. Fig. 5 illustrates that in the model for the Ag(Cu) system, two effects facilitate trapping at high concentrations. The interface diffusivity drops by a factor of two as we go from the melting point of silver to the eutectic temperature, thus making the redistributive reaction more difficult while not sensibly affecting the growth mobility. In addition, the driving force for redistribution is smaller at high concentrations.

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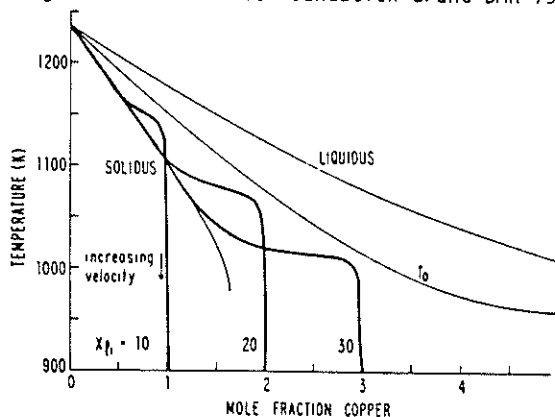


Fig. 3 Interface temperature and solid composition for fixed  $X_{li}$  in Ag(Cu). For a given liquid composition  $X_{li}$  at the interface, the solid composition increases and the interface temperature drops as the velocity is increased.

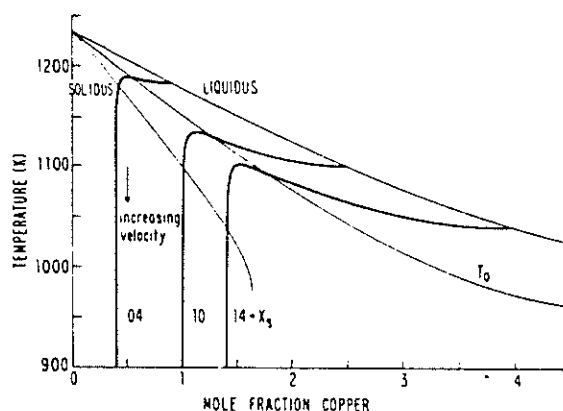


Fig. 4 Interface temperature and liquid composition at interface for fixed  $X_s$ . When the  $T_0$  line is crossed the diffusionless transformation becomes thermodynamically possible, but it does not occur until some distance beyond.

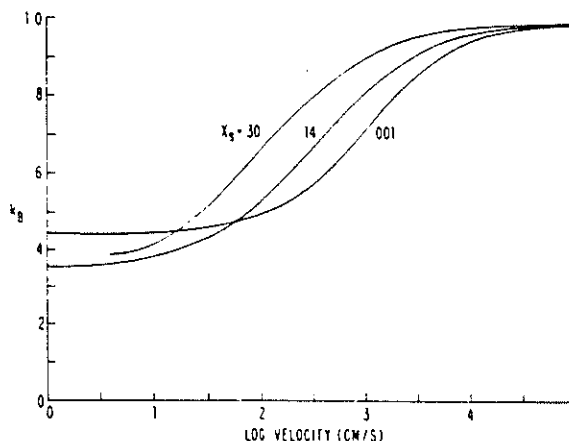


Fig. 5 Segregation Coefficient vs. Velocity for Dilute and Concentrated Alloys of Cu in Ag. In this system, two effects facilitate trapping at higher concentrations. The interface diffusivity drops and the driving force for redistribution drops.

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